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Hydrothermal carbonization: combination of heat of reaction measurements and theoretical estimations

An experimental procedure using a calvet differential scanning calorimeter

**Tammo Rebling · Petra von Frieling ·
Jörg Buchholz · Thomas Greve**

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Abstract Experimental data for the heat of reaction during the hydrothermal carbonization (HTC) of biomass are scarce. Theoretical approaches can be found in literature, but the values are in a wide range. Up to now, there is no publication that presents a combination of theoretical estimation and experimental determination of the heat of reaction. The comparison is very important, for example to improve and validate the theoretical approaches. In this study, a new experimental setup at a heat flow DSC in temperature scanning mode is presented. It allows for the first time a comparison between measured and estimated values for the heat of reaction from the same HTC experiment: a sample mass of about 1.25 g, composed of biomass from a nature protection area and water, is carbonized while the heat of reaction is recorded. The usage of a removable glass container as inset allows to balance the process. The sample volume allows CHN analysis of the HTC-coal for theoretical estimations of the heat of reaction. The results show that the setup leads to reproducible results for the recorded heat flows and the CHN composition of the HTC-coal. Compared to the experimentally determined value for the heat of reaction of biomass in HTC process of $(-715.1 \pm 15.3)\,\mathrm{J\,g_{daf}^{-1}}$, the estimation for the heat of reaction leads to an overrated value, even if the dissolved organic matter (dried on the coal) is considered in the energy balance.

Keywords DSC · Temperature scanning · Heat of reaction · Calculation · HTC

Abbreviations

Cel	Cellulose
daf	Dry and ash-free
DOM	Dissolved organic material
DSC	Differential scanning calorimetry
HHV	Higher heating value
HTC	Hydrothermal carbonization

Introduction

In the last decade interest on biomass conversion to coal-like substances increased rapidly. In particular, the thermochemical conversion of water-bathed biomass at temperatures between 180 and 250 °C got more attention. Several published studies summarized this process as hydrothermal carbonization (HTC) [1–3]. In a sealed reactor the biomass is hydrolyzed and dehydrated under an autogenous pressure. Additionally a decarboxylation occurs. In the following reactions of polymerization and aromatization the solid coal-like product is formed. Depending on the intended product quality there is a residence time of several hours. In general the hydrothermal carbonization is proved as an exothermal process [1, 4, 5]. Although the number of publications regarding the HTC increased, there is still a lack of thermodynamic studies.

T. Rebling (✉) · P. von Frieling · J. Buchholz
University of Applied Sciences Osnabrück, Osnabrück, Germany
e-mail: t.rebling@hs-osnabrueck.de

P. von Frieling
e-mail: p.von-frieling@hs-osnabrueck.de

J. Buchholz
e-mail: j.buchholz@hs-osnabrueck.de

T. Greve
Carl von Ossietzky University Oldenburg, Oldenburg, Germany
e-mail: thomas.greve@uni-oldenburg.de

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Most known studies estimated the heat release (mostly given as enthalpy of reaction ΔH_R) of HTC by simplified stoichiometric methods of mass and energy balances. The calculated values in the literature show depending on the used biomass and the method of calculation a range of about $-5.8\,\mathrm{MJ\,kg_{feed,dry}^{-1}}$ up to zero [1, 6, 8]. The value of $-5.8\,\mathrm{MJ\,kg_{feed,dry}^{-1}}$ was calculated by assuming that the value for the released heat can be calculated by difference of the calorific values of glucose and the thereof produced coal [1]. The value of about zero $\mathrm{MJ\,kg_{feed,dry}^{-1}}$ is based on a calculation from the heats of formation. Therefore, detailed analysis of reactants (loblolly pine) and products (solid, liquid, and gas) had been performed [6]. As this calculation neglects the exothermic formation of water, it underrates the heat of reaction [7]. Therefore, the method of calculation as well as the type of biomass lead to the large range of values, which is not acceptable.

Only in a few publications experimental methods were applied under hydrothermal conditions [5, 9, 10]. The experimentally determined caloric effects were about $-1.07\,\mathrm{MJ\,kg_{cel,daf}^{-1}}$ and $-0.76\,\mathrm{MJ\,kg_{wood,daf}^{-1}}$ [5, 10]. There, a power compensated DSC was used in isothermal mode. Due to the long-lasting isothermal measurements it was difficult to define a certain peak of the exothermal reaction in heat flows less than 5 mW and spread over a time of up to 6 h [10]. However, although it could be shown that the temperature influences the reaction kinetics (the shape of the heat flow curve), the total enthalpy of reaction was not affected [5]. Detailed information on the temperature depending heat release are still not provided and the results of theoretical estimations are unsatisfactory.

In addition, only masses of about 4 mg of biomass were used due to the instrumental specifications of the chosen DSC with a volume of the pressure capsules of only 30 µl. With these low masses neither a direct measurement of the calorific value nor an elemental analysis to calculate the higher heating value (HHV; according to [11]) could be applied. The HHV is used in most papers to calculate the enthalpy of reaction by the simplified law of Hess and mass balance [1, 4, 8], what was not possible here [5, 9, 10]. Therefore, there are no publications comparing the experimental data with the calculations from the same HTC experiment by a reproducible method.

A promising measuring system seems to be the heat flux DSC. This system is known for larger sample volumes (that allows CHN analysis of the product) and a high sensitivity per volume unit [12], whereas the heating rates are lower than in power compensated DSC [5, 9, 10]. For any measurement in a DSC a steady state is needed. This is mostly accomplished by operating in isothermal mode (constant heating rate = 0) or with a constant heating rate (>0). With the chosen heat flux DSC, only low heating rates of maximum 2 K min^{-1} obtain reproducible results. With these low rates, the isothermal mode would lead to long times to heat up to the examined temperature. In this heat-up phase the signal could not be evaluated although the exothermal reaction of the HTC might have started. Hence the accuracy of this isothermal method decreases with raising temperature.

Therefore, in this study an experimental setup for HTC heat of reaction measurements is illustrated, which allows experimental measurements and simultaneously theoretically estimations. For the measurement a C80 calorimeter (Setaram) is used in temperature scanning mode, which allows a hydrothermal reaction within full mass balance using removable glass container. This setup, as shown in Fig. 1, additionally protects the cylindric metall cell from direct corrosion and deposits. At present, no comparable experimental setup for HTC heat of reaction measurements is known to the authors.

To prove the accuracy of this experimental setup and to compare the estimated and experimental values of the heat of reaction from one experiment, five steps of experiments and calculations were performed:

1. The impact of using a glass container.
2. Heat flow correction by subtracting the effect of the water.
3. Reproducibility of heat flow detection and the HTC process.
4. Determination of the heat of reaction.
5. Theoretical estimation and comparison to experimental values of the heat of reaction.

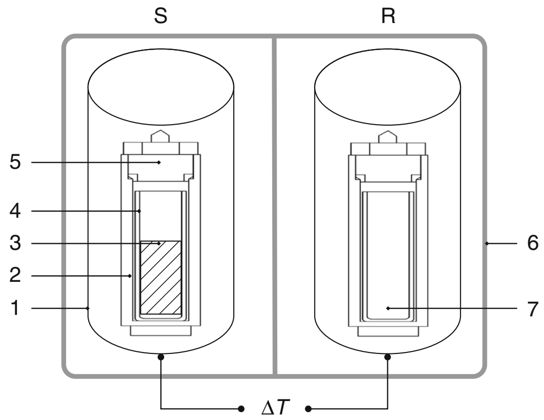

Fig. 1 The characteristic schematic drawing of a calvet heat flux DSC, using glass container for balancing the HTC experiments for sample (S) and reference (R) cell. 1: 3D-heat flux sensor; 2: high pressure cell (S60/1413); 3: sample suspension; 4: glass container; 5: cap of the high pressure cell; 6: furnace; 7: empty glass container

Experimental section

For all calorimetric measurements a heat flux DSC from Setaram (C80) was used. The DSC was calibrated by a Joule effect cell from ambient to 300 °C. The temperature depending sensitivity is characterized by the polynomial coefficients (μV mW^{-1}), which were implanted in the used software (Calisto Processing and Data Acquisition v.1.12). In the experiments to determine the impact of using glass container, standard normal pressure cells (S60/1413) with an 12.5 cm^3 stainless steel body were used to determine the enthalpy of fusion ΔH_{fus} of tin and indium (constant pressure). For all hydrothermal measurements the DSC was used with stainless steel high pressure cells (S60/1416) with an 8.5 cm^3 body (pressure limit 100 bar). In this case, the volume was held constant, therefore the heat of reaction ΔU_{R} is determined. Additionally, for the presented experiments, specific flat top borosilicate glass containers (outside diameter (11 ± 0.18) mm; wall thickness (1 ± 0.04) mm; length (53 ± 1) mm; volume 3.2 mL) were used. In either case, the measured heat flow signals were recorded by Calisto Data Aquisition. Further data analyses were performed with Calisto Processing and Gnuplot (4.6).

The impact of using glass container

By using additional glass container in the sample and the reference cell, the masses of reactant and product can be weighed and therefore be balanced. This allows calculations of the caloric value and thereby a theoretical determination of the heat of reaction by the simplified law of Hess as done by [1, 4, 8]. On the other hand, this changes the thermal properties (e.g., thermal conductivity, specific heat, mass) of the experimental setup. This impact of glass container on the caloric measurements was analyzed by the determination of the enthalpy of fusion of indium and tin. The tin and indium were standard grade chemicals from Sigma Aldrich. The aluminum oxide as socket for tin and indium was purchased from Riedel de Haën.

Experimental procedure

Correspondent to the recommendation of the manufacturer, the samples were placed on a defined mass of Al_2O_3. The same mass of Al_2O_3 was placed in the glass container of the reference cell. In each case, the samples (525 mg In; 451 mg Sn) were heated up with 0.1 °C min^{-1}. The measurements were performed in duplicates.

Evaluation method

According to ISO 11357-5:2013 the enthalpy of fusion was determined by integration with a horizontal baseline of the obtained peaks.

Heat flow correction by subtracting the effect of the water

In an experimental setup under HTC conditions, the effect of mass and specific heat of water predominates the potential of the effects caused by the biomass (only about 20 % of the sample mass). Furthermore, the considered heat flow signals include the change of the specific heat of water by changing temperature and pressure during the temperature profile. In general, there are two common procedures to correct heat flows: As specified in ISO 11357-5:2013, a reacted sample is measured a second time. In case of no further reactions taking place during the second measurement, the first signal can be corrected by the second signal. The main advantage of this correction procedure is the consideration of the (changed) resulting specific heat of the products, which were formed during the first measurement. But due to the heterogeneous sample suspension and in particular the condensed water in the gap of glass container and the high pressure cell, a further measurement could not accomplish the desired results. Therefore, this procedure is neglected in the following considerations. As first reliable procedure for the given setup, there is the option to fill the reference cell with the same mass of a filling element, used in the sample cell. Thus, the mass and thermal effects of this filling material were reduced and the thermal effects of the sample material were revealed (ISO 11357-1:2009). For hydrothermal measurements this experimental setup was already used [5, 10]. At a power compensated DSC the reference cell is filled with the same mass of water as used in the sample. Additionally, the raw signal was corrected by a zeroline subtraction, which corrected the heat flow signal caused by the asymmetry of the measurement system. The workload for the latter setup is about twice as high as the first one where only one cell has to be prepared. Therefore, a new experimental procedure is developed.

For HTC experiments with the same amount of water, a reference experiment with the same setup, but only water instead of the water biomass suspension, is done once as a duplicate measurement. The resulting curves can be subtracted from all following HTC heat flow curves. Additionally, in these experiments only one pressure cell has to be handled (e.g., weighing, opening, cleaning). Therefore, the probability of cell leakage and the time effort per measurement is lower as only one additional experiment has to be done. In the following the latter two procedures are checked and discussed to reduce the water effects in the raw heat flow signal and to define a clear signal which is mainly caused by the caloric effects of the HTC reaction.

Experimental procedure

Two different types of experiments were conducted in duplicates, in an experimental setup as shown in "Reproducibility of heat flow detection and the HTC process" section.

- *Procedure I* The first experiment is performed according to ISO 11357-1:2009. Whereas in the sample glass container 0.25 g biomass from landscape management (air dried and grinded to 0.2 mm) and 1 mL distilled water is added, the glass container of the reference cell is also filled with 1 mL water. In two further experiments, the zerolines of the empty high pressure cells are determined. For the evaluation, the mean heat flow signal of the two conducted zeroline experiments is subtracted from the raw signal of the measurement.
- *Procedure II* The second approach is performed according to the first one, but the reference glass container now remains empty. Additionally to this measurement, there is a duplicate of water experiment performed: In spite of biomass, only 1 mL of water is used in the sample cell, while the reference cell stays empty and the experimental conditions are the same. For the evaluation, the mean heat flow of the two conducted water experiments is defined. Afterward, the mean heat flow of the water experiment is subtracted from the raw signal of the biomass experiment.

Evaluation method

The resulting heat flows of both procedures were evaluated in their characteristic data points.

Reproducibility of heat flow detection and the HTC process

In the third part, the carbonization of biomass from a nature protection area (air dried and grinded to 0.2 mm) was checked for reproducibility. Therefore, the heat flows were recorded, corrected (Procedure II), and mass balances were performed.

Experimental procedure

The sample glass container was filled with 0.25 g biomass and 1 mL of a 0.08 molar solution of citric acid. The solid content of the homogenized suspension was about 19 % at a pH value about 3.4. After sample preparation, the filled glass container was placed in the sample cell, whereas an empty glass container was set in the reference cell. Both cells were tightened with a torque of 20 Nm and installed to the C80 calorimeter. A linear heating rate of 1 °C min^{-1}from 30 °C to the maximal calorimeter temperature (300 °C) was applied. After reaching 300 °C, the system cooled down continuously for 6 h. While the total time effort for one measurement is at least 11 h, the biomass was about 6 h above 100 °C. The tightness of the ambient cells was checked by determination of the mass difference.

Mass balances and analytics

Both, biomass and products were analyzed as shown in the following:

- The **water content** was determined according to the oven dry method (ISO 14774-2:2003). Raw biomass and product suspension in the glass container were dried at 105 °Cuntil the mass was constant. Therefore, the dissolved organic matter is bound in the solid and can be balanced, too. The lost mass in relation to the sample mass was defined as water content (given in percent by mass).
- The **solid yield** ω_{yield} of the carbonization was calculated according to Eq. (1) and defined in percent by mass. Both product mass m_{product} and mass of biomass m_{biomass} were referred to the dry mass.

$$\omega_{\text{yield}} = \frac{m_{\text{product}}}{m_{\text{biomass}}} \cdot 100 \tag{1}$$

- The **ash content** of the biomass $\omega_{\text{ash,biomass}}$ was determined according to DIN 14775-2004-11 and was specified as percent by mass ash per dry mass. Due to the small sample mass after carbonization, no ash analyses could be performed. Therefore, the ash content of the product was calculated in two steps: First, the total mass of ash m_{ash}, in the used biomass (with mass m_{biomass}) was calculated, assuming that no ash is lost during the measurement and the drying of the product mixture:

$$m_{\text{ash}} = \frac{\omega_{\text{ash,biomass}}}{100} \cdot m_{\text{biomass}} \tag{2}$$

In the second step, the calculated mass of ash was referred to the mass of dried product m_{product} so that the ash content of the product $\omega_{\text{ash,product}}$ was specified in percent by mass:

$$\omega_{\text{ash,product}} = \frac{\omega_{\text{ash,biomass}}}{\omega_{\text{yield}}} = \frac{m_{\text{ash}}}{m_{\text{product}}} \tag{3}$$

- The **elemental composition** of the dried biomass and the coal-like product was determined via Vario EL

(Elementar) elemental analyzer. For every sample the percent by mass amounts of C, H, and N were analyzed. The mass fraction of oxygen in the samples was calculated via Eq. (4), using each percent by mass amounts, neglecting the oxygen which is bound in the ash (e.g., $CaCO_3$).

$$O[\%] = 100 - C[\%] - H[\%] - N[\%] - \mathrm{ash}[\%] \quad (4)$$

- The **higher heating value** (HHV) of the biomass was analyzed via bomb calorimeter (IKA C200) according to DIN 51900-2. Due to the small sample mass of the coal (less than 1 g), the HHV of the products could not be analyzed. Therefore, the HHV value was calculated via the numerical formula of Channiwala [11], but without sulfur:

$$\begin{aligned}\mathrm{HHV}\left[\mathrm{MJ\,kg^{-1}}\right] &= 0.3491 \cdot C[\%] + 1.1783 \cdot H[\%] \\ &\quad - 0.0151 \cdot N[\%] - 0.1034 \cdot O[\%] \\ &\quad - 0.0211 \cdot \mathrm{ash}[\%] \end{aligned} \quad (5)$$

The accuracy of Eq. (5) was tested for different HTC coals (same biomass, different temperatures, and reaction times). For each sample the difference between experimental and estimated heating value was calculated. The arithmetic mean of the differences was about 2 %. Therefore, the sulfur content of less than 0.2 % has no crucial impact.

Evaluation method

The heat flow signals and each elemental composition were compared and tested for their reproducibility.

Determination of the heat of reaction

To determine the heat of reaction according to ISO 11357-5-2013, the area below the peak of the corrected heat flow signal has to be calculated. Therefore, a baseline and two integration limits have to be defined. Due to the fact, that the recorded heat flows have no full peak in the considered temperature range (like the melting peak of tin), and therefore a defined temperature interval for the reaction, the points for the integration have to be defined with the following requirements:

First, the integrations limits have to be defined reproducibly for different measurements (e.g., different biomass or reaction additives) to gain comparable results. Second, the limits must be located within a constant heating rate [12]. Third, to include all the released heat within the hydrothermal carbonization, the integration interval has to be as large as possible. Only if all heat effects are considered, the composition of the coal is reflective of the experimental determined heat and a comparison to the theoretical estimated heat release as shown in "Theoretical estimation and comparison to experimental values of the heat of reaction" section can be done.

As there is a constant heating rate at 100 °C and according to first observations of hydrothermal reactions of biomass at about 100 °C [13], the integration starting point is set to 100 °C. The integration end is set to the end of the constant heating rate at a temperature of about 291 °C. This endpoint is determined for each measurement, since there is the end of the constant heating rate. The interpolated baseline is constructed as a first point horizontal line. With this line, there is an area defined for integration. The fraction of that integration represents the heat of reaction. With the chosen integration limits, the boiling peak of water is part of the integration area. Due to its small amount of the total integration area (less than 0.3 %), the boiling peak is neglected in the further evaluation.

As it is known, the hydrothermal reaction produces a gaseous phase [2]. Due to this gaseous phase, there are changes in the pressure within the used high pressure cell. Therefore, the resulting heat of the applied measurement is defined as the internal energy ΔU_R. In literature, the heat release is mostly given as the enthalpy ΔH_R, which is linked via the volume work pV and ΔU_R according to:

$$H = U + pV \quad (6)$$

Theoretical estimation and comparison to experimental values of the heat of reaction

After analyzing the products, calculations can be done to estimate their energy contents. Summing up the energies, the missing energy is assigned as the enthalpy or heat of reaction. In literature, different methods were used to estimate the enthalpy of reaction of the HTC. Most methods are based on Hess's law, in which the enthalpy of a chemical reaction is the difference of the sum of all product and reactant enthalpies of formation H_f°:

$$\Delta H_R^\circ = \sum_{\text{products}} \Delta H_f^\circ - \sum_{\text{reactants}} \Delta H_f^\circ. \quad (7)$$

The calculation according to Eq. (7) can only be performed for a fully known reaction. As the HTC of biomass is known as a reaction network with a lot of different intermediates and products [2, 14, 15], simplifications have to be performed. The most extensively approach was performed by [6] for wet torrefaction of wood, including glucose, 5-hydroxymethyl furfural (5-HMF), and acetic acid [6]. Even this approach requires strong simplifications. As it needs a lot of effort for the balance performed [6], in most studies further simplifications have been applied. For example, the most cited approach is by Bergius [16]: reducing the HTC of cellulose on the dehydration and decarboxylation of the initial biomass, a reaction equation is generated. Therefore, the main products are coal, CO_2 and H_2O, whereas the formed dissolved organic material (DOM) and further gaseous compounds like CH_4 are neglected. By using the combustion enthalpy in form of the HHV (instead of the enthalpies of formation) and the mass balance, a resulting heat was calculated:

$$\begin{aligned}[C_6H_{10}O_5]_4 &\longrightarrow C_{21}H_{16}O_2 + 12\ H_2O + 3\ CO_2 \\ \Delta H_R &= -1191.6\,\mathrm{kJ\,mol^{-1}} \\ &= -1840\,\mathrm{J\,g^{-1}}\end{aligned} \tag{8}$$

In this approach, the energy which is stored in the unconsidered byproducts of the HTC (e.g., DOM or combustible gases) is neglected. As known from [8] up to 30 % of the carbon of the feed could be found in the process water, depending on the process parameters and feed. Therefore, the calculated heat release is systematically overrated [5].

To reduce this overestimation, in this study, the theoretical heat of reaction is estimated in the style of Bergius with an additional aspect: According to Eq. (8), the biomass is converted into coal, CO_2 and H_2O. Assuming that due to the drying of the coal slurry, all dissolved organic material is bound in the analyzed coal, an equation can be formed for each performed carbonization:

$$C_aH_bN_cO_d \longrightarrow m \cdot C_wH_xN_yO_z + p \cdot H_2O + q \cdot CO_2. \tag{9}$$

As the equation system for the conversion of biomass is reduced severely, the balances for the elements and masses are not fully closed. For a better calculation in the following, the reaction equation is balanced with preference on the mass, followed by C, O, and N. The ratio of H is less important here due to its low molecular mass. The enthalpy ΔH_R^{calc} of this reaction system is estimated according to Eq. (10), each based on the dry and ash-free mass of the used biomass $m_{biomass}$, the resulting mass of coal $m_{product}$ and the respective HHV.

$$\Delta H_R^{calc} = \frac{m_{product}}{m_{biomass}} \cdot HHV_{product} - HHV_{biomass}. \tag{10}$$

Results and discussion

The impact of using glass container

The glass container will cause a delay in heat transfer [12]. Therefore, the shape of the heat flow signal will change, but not the size of the area below the curve, which is used to determine the heat of reaction. As the maxima of these curves will be used as indicator for the temperatures of exothermic reactions, the impact on the shape of the measured curve has to be investigated. This is exemplary done by determining the enthalpy of fusion of indium and tin. Both substances have the melting point within the HTC-temperature range. Additionally, the absolute difference to literature values can be determined. The results are shown in Figs. 2 and 3, measured without Al_2O_3 socket for a better visualization. For standard caloric measurements, the peak temperature maximum (T_P) and the peak width are not suited to characterize the peak geometry. This is caused by their strong dependence on parameters like heating rate, thermal conductance or mass [12]. Nevertheless, in this study, the peak geometry is characterized in Table 1 to determine the impact of the glass container. The value for ΔH_{fus}^a in Table 1 is measured with Al_2O_3.

As expected, the use of the glass containers resulted in a decrease of the heat flow signal due to the lower thermal conductivity of the system ($\lambda_{glass} = 0.72\,\mathrm{W\,K^{-1}m^{-1}}$, $\lambda_{steel} = 15\,\mathrm{W\,K^{-1}m^{-1}}$ [17]). The mean values of the two performed measurements (deviation each less than 1 %) show, that the temperature of the beginning of the melting (T_i) is influenced by the glass container less than 0.2 %. As known from literature, the peak maximum (T_p) is more affected by a changed experimental setup [12]. In this case, T_p drifted due to the use of glass container by about 1.0 °C. These differences in the shape of the peak influence the peak area ΔH_{fus}^a up to 1.8 %. In this study, the difference between literature values (ISO 11357-1:2009) and the determined values with glass containers is overall less than 2.4 %.

In summary, there is an effect on the heat transmission due to the glass container. In case of the two considered temperatures up to 235 °C, the effect on the peak area is about 1.8 %. For the HTC measurements it is assumed, that

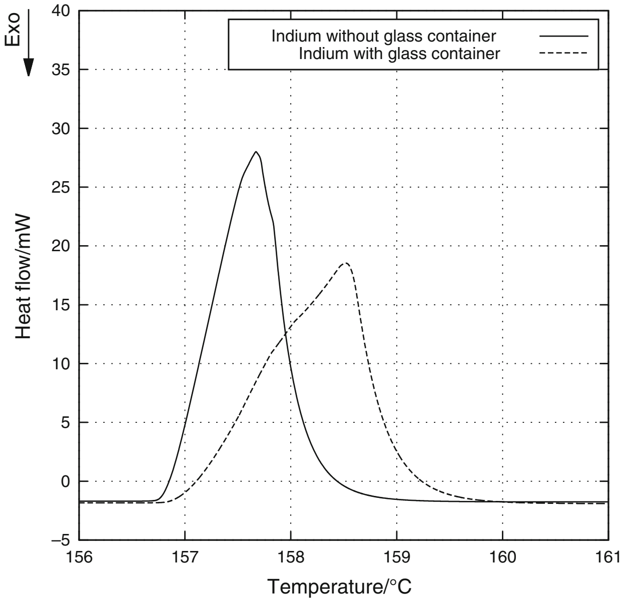

Fig. 2 Impact on the peak shape using glass container (*dashed line*) at the melting point of indium

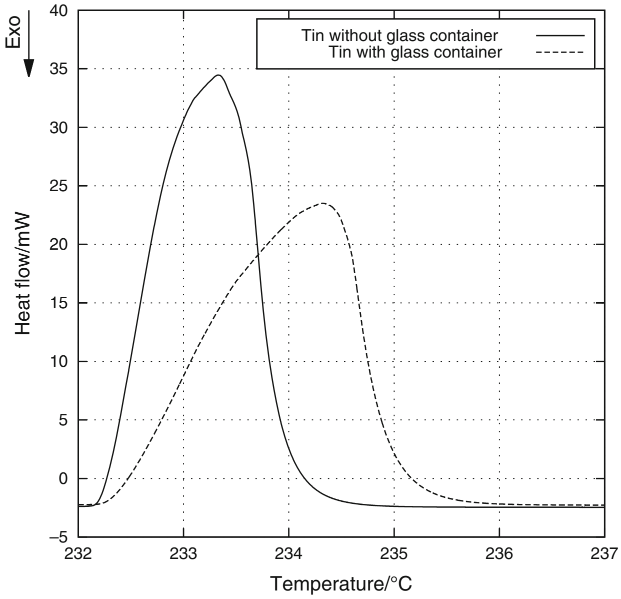

Fig. 3 Impact on the peak shape using glass container (*dashed line*) at the melting point of tin

Table 1 Results from the measurement at the melting point (ΔH_{fus}) of indium (In) and tin (Sn) showing the impact of the use of glass container for the beginning of the peak (T_{i}) and the peak maximum (T_{p}). For each case the difference Δ_{glass}, caused by the glass container, is calculated

	T_{i}/°C	T_{P}/°C	$\Delta H^{a}{}_{\mathrm{fus}}/\mathrm{J\,g^{-1}}$	$\Delta H^{b}_{\mathrm{fus}}/\mathrm{J\,g^{-1}}$
In	156.39	157.67	28.75	28.62
$\mathrm{In}_{\mathrm{glass}}$	156.48	158.46	28.24	–
Δ_{glass}	0.09	0.79	0.51	–
Sn	231.42	233.32	58.99	60.40
$\mathrm{Sn}_{\mathrm{glass}}$	231.82	234.31	59.07	–
Δ_{glass}	0.40	1.01	0.08	–

[a] Experimental determined value for the enthalpy of fusion

[b] Reference value for the enthalpy of fusion (ISO 11357-1:2009)

this influence is also valid in the temperature range up to 300 °C.

Heat flow correction by subtracting the effect of the water

As the correction procedure according to ISO 11357-1:2009 (procedure I) has a high workload for the applied hydrothermal measurements at the C80 calorimeter, a new experimental procedure with a lower workload (procedure II) is developed and evaluated.

Procedure I This first approach is applied with a filled reference glass container, according to ISO 11357-1:2009, at which the raw signal is corrected by a zeroline subtraction.

Procedure II In this second approach, the reference glass container is empty. The correction of this experiment is performed by the subtraction of the curve curve of a performed water experiment (in duplicate; same setup but without biomass). This curve can be used for all following measurements and therefore, leads to the desired reduction of the workload. The corrected signals of the two procedures are plotted in Fig. 4.

As expected, the raw signals differ in amplitude and shape (not shown). After the correction the signals get similar to each other, as shown in Fig. 4. The similarity is given for the virtual baseline (up to 100 °C) as well as the total amplitude $\Delta \mathrm{dQ}/\mathrm{d}T$. The characteristic data points of both experimental approaches are listed in Table 2. At the three characteristic peaks at the temperatures T_{P200}, T_{P260} and T_{P290}, the deviation between the values of procedure I and procedure II is within the error range and the difference between the curves is in agreement with the reproducibility of Fig. 5.

The results show that a water experiment correction could achieve almost the same heat flow signal as a measurement with filled reference glass container according to ISO 11357-1:2009. The main presupposition for the applied water correction is a steady measurement system. Therefore, water tests have to be applied regularly to check the used water correction experiment.

However, the reproducibility of thermal effects during HTC is discussed in the following, using procedure II.

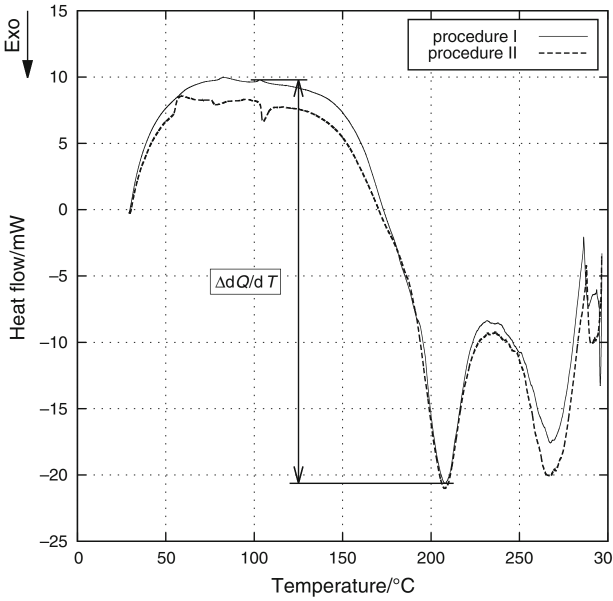

Fig. 4 Corrected heat flow signals of HTC experiments, using procedure I (corrected according to ISO 11357-1:2009) and procedure II (corrected by an additional water experiment)

Table 2 Temperatures T_{P200}, T_{P260} and T_{P290} of the characteristic peaks in the heat flow signal for method I (reference glass container filled with water) and method II (raw signal corrected by water experiment) of duplicate measurements

	T_{P200}/°C	T_{P260}/°C	T_{P290}/°C	$\Delta dQ/dT/mW$
Procedure I	207.9	269.3	288.0	31.1
	±0.3	±3.7	±3.3	±1.4
Procedure II	207.5	268.1	288.4	30.5
	±0.5	±1.9	±1.1	±2.6

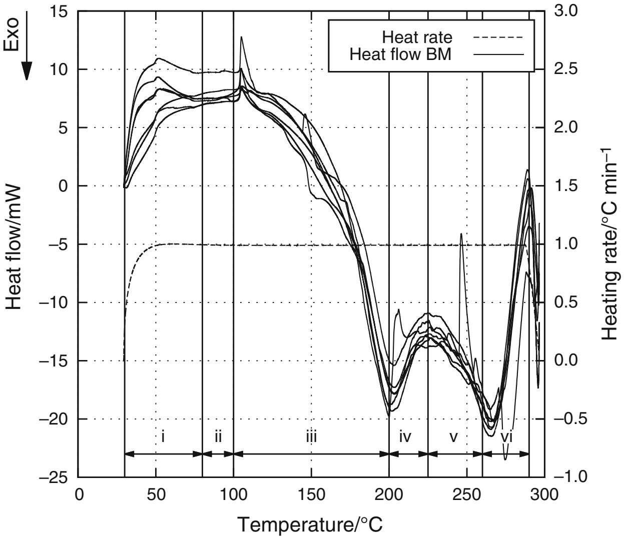

Fig. 5 Corrected signals of reproduced measurements of the hydrothermal carbonization of biomass under same conditions in a heat flux differential scanning calorimeter within a constant heating rate

Reproducibility of heat flow detection and the HTC process

As the effect of glass container and the correction method are verified now, measurements of HTC experiments are performed in the heat flux DSC to prove the reproducibility of the method.

Evaluation of the recorded heat flow signals

The corrected heat flows are summarized in Fig. 5. The heat flow signals show a similar shape, which can be divided into six phases:

(i) 30–80 °C: The system is heated up, each with little inevitably differences in mass and temperature.

(ii) 80–100 °C: A stable heating rate is reached. There is no change in the specific heat, therefore, the signals are almost parallel.

(iii) 100–200 °C: The endothermic peak T_{P105}at a temperature of about 100 °C has its origin in the pressure build-up due to the phase shift of water. At about 150 °C all signals are getting a negative heat flow and indicate an exothermal peak (T_{P200}) at about 200 °C.

(iv) 200–225 °C: At the further raise of temperature, there is a local maximum of the heat flow at about 225 °C.

(v) 225–260 °C: The local maximum in the heat flow of about 225 °C is followed by second exothermal peak (T_{P260}) at about 260 °C.

(vi) 260–290 °C: The end of the constant heating rate is reached at 290 °C. At this temperature all heat flows have reached a local maximum peak (T_{P290}) caused by the end of the constant heating rate. T_{P290} is therefore no chemical reaction caused peak.

Although some of the signals show artifacts (spurious peaks, probably caused by thermal effects of the heterogeneous and not mixed slurry in the cells) and a vertical shift, the analyzed heat flows follow the same trend. The characteristic data points of these heat flows are summarized in Table 3. For the exothermal peak T_{P260} the deviation of about ±3.5 °C is caused by one experiment with an artifact at the same temperature. Excluding this experiment, the peak mean is about (265.7 ± 0.9 °C). Altogether, the temperature deviation is for the reproduced experiments less than ±1.5 °C. Furthermore, the HTC is known as a reaction, which lasts for several hours [1, 2]. In case of the applied heating rate of 1 °C per minute in this temperature scanning setup, there is a considered time above 100 °C of about 3.3 h. This is of the same order as the reaction time in the experiments of [5], where the reaction time of 3.5 h is defined as time at the temperature 240 °C. Therefore, the reaction times of the two methods are not directly comparable. As [5] showed, the main exothermal effects of the carbonization of cellulose occur during this first 3.5 h [5]. With the knowledge of the Arrhenius law, for the experimental setup used in this study, it can be assumed, that the main thermal effects of the biomass suspension were recorded during the considered time and temperature interval. This aspect will be picked up in the last section, as the elemental composition

Table 3 Statistics of the four temperatures T_{Pi} at the characteristic points in the shapes of the seven reproduced signals, where i is the rough temperature of the point

	T_{P105}/°C	T_{P200}/°C	T_{P260}/°C	T_{P290}/°C
Mean	105.1	202.1	266.9	289.9
Deviation	±0.3	±1.4	±3.5	±1.2

of the product shows the progress of the reaction. It can not be excluded, that further thermal effects appear during the cooling phase. They could not be considered in this experimental setup.

Altogether, the horizontal deviation of the peaks of less than 1 % underlies the thermal conductivity effects caused by the use of glass container. In some experiments the heat flow is disturbed by artifacts (Fig. 5). This might be caused by different effects: The most probable reason can be seen in the experimental setup. The heterogeneous sample could not be stirred in the DSC cell. Furthermore the reaction temperature (up to 300 °C), the vapor pressure (up to 86 bar) and a generation of gaseous byproducts CO_2 or CH_4) have an impact on the suspension. Influenced by these factors, fluctuations in the sample suspension are likely. This might be comparable with a delay in boiling which might explain the pushed up solids in the glass container after each measurement. Sample fluctuations would lead to abrupt changes in the heat transmission, artifacts in the heat flow and sometimes to solid residues at the cap of the cell.To be sure that a hydrothermal reaction took place, despite the sample fluctuations of the products, the chemical composition of the products will be considered next.

Evaluation of the chemical analysis

Just as well as the measured signals, the mass balance and analytics of the products show the reproducibility of the used method, as summarized in Table 4. The deviation of the considered parameters (yield and elemental composition) are below 1 %. Due to the slow cool down, there is always condensed water between the glass container and the steel wall of the cell. Even this amount of condensed water is reproducible.

Due to the carbonization, the carbon content of the biomass (about 47 %) increased up to 68 % in the solid product. By knowing the elemental composition of the used raw biomass before carbonization and the composition of the dried product, the characteristic atomic O/C and H/C ratios were calculated. In Fig. 6 the atomic ratios of the biomass and the products were plotted in comparison to atomic ratios of data from hydrothermal carbonization for comparable biomasses found in literature (Van Krevelen Plot).

Table 4 Results of performed analysis and mass balance of seven reproduced experiments. These values refer to the dry mass

	Mean	Deviation
ω_{yield} (%)	54.90	± 0.02
$\omega_{\text{ash,product}}$ (%)	6.37	± 0.18
C (%)	68.08	± 0.81
H (%)	5.39	± 0.15
N (%)	2.99	± 0.05
O (%)	17.17	± 0.84
Condensed H_2O (g)	0.201	± 0.062
HHV (MJ Kg^{-1})	28.16	± 0.40

Characteristic for hydrothermal reactions is a shift within the Van Krevelen Plot during the carbonization: The biomass is arranged at the top on the right-hand side, with a relatively high O/C and H/C ratio. During the HTC, these ratios are decreased due to reactions of decarboxylation and dehydratation [2, 15]. Therefore, the data points for the products are moved down and to the left.

In comparison to the values of other HTC products found in literature, the atomic ratios of the products of the performed experiments are in the same range. As the temperature T goes up to 290 °C in the experiments the values are, as expected, in the region of maximum dehydration and decarboxylation in this range of comparable HTC data. This leads to the conclusion that HTC has taken place in the experiments.

In summary, the heat flow signals are reproducible. The containing exothermal peaks and the chemical composition of the products are reproducible too. The values from analysis show a small range of deviation. The next step is to determine the heat of reaction.

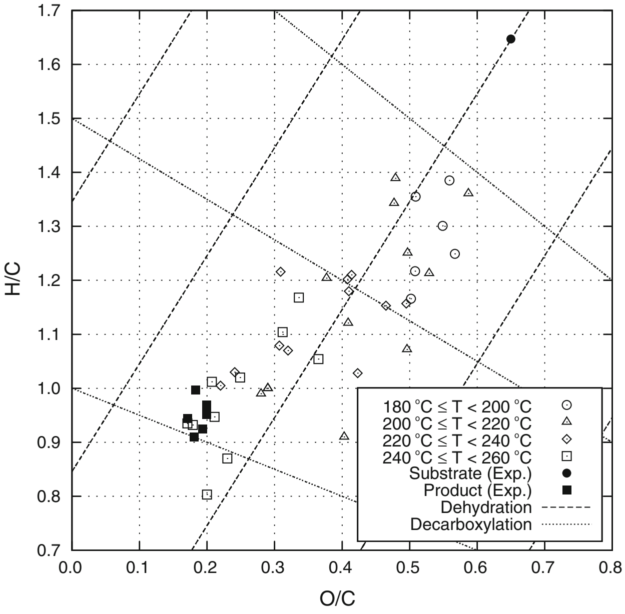

Fig. 6 Van Krevelen plot: Atomic ratio H/C over the atomic ratio O/C of the used biomass and the products after HTC. Data from literature with a similar type of biomass (e.g., grass, leaves, herbs) and 180 °C ≤T ≤ 250 °C is plotted additionally [2, 3, 14, 18–23]. The *dashed lines* show the route of dehydration, the *dotted lines* the way of decarboxylation

Determination of the heat of reaction

The results of the reproducibility experiments show, that there is a heat release during the hydrothermal carbonization. As presented in Fig. 7 the integration was performed in a temperature range between 100 and 291 °C. The heat was referred to the dry and ash-free initial biomass. In the example, ΔU_{R} was about $-712\,\mathrm{J\,g_{daf}^{-1}}$.

The arithmetic mean of the seven replicate measurements is about $-701\,\mathrm{J\,g_{daf}^{-1}}$ with a deviation less than 4 % (Table 5). Excluding the two mentioned experiments with large artifacts, the mean value for the heat of reaction is about $-715\,\mathrm{J\,g_{daf}^{-1}}$ with a deviation of about 2 %. Therefore, in the following only the five experiments without artifacts are used. Although there appear artifacts in the signals and the carbonization is performed in a small unstirred container, this method gives reproducible results.

Compared to the ΔH_{R} data of cellulose and wood by Funke in Table 5, the determined ΔU_{R} in this study is smaller. Possible reasons are as follows:

First, the ΔU_{R} has not considered the volume work according to Eq. (6). Due to the fact, that the volume of the produced gas is not measured, ΔH_{R} and ΔU_{R} can not be converted directly. Only using a reaction equation (as done in the last section), a conversion of both values is possible. However, the lack of consideration of the volume work overrates the (absolute) value for ΔU_{R} and a further comparison with literature data for ΔH_{R} is not possible due to the scarce of information.

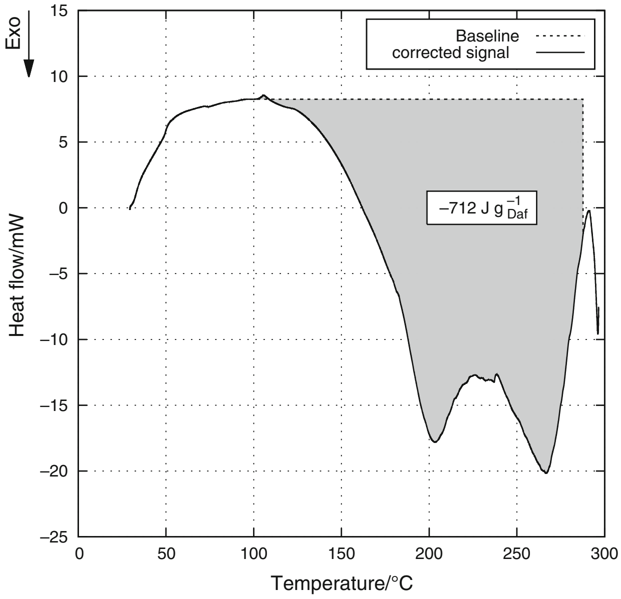

Fig. 7 Example for the determination of the heat of reaction by first point horizontal integration from 100 to 291.2 °C of a corrected heat flow signal (method II). The heat of reaction is referred to the dry initial mass of biomass

Table 5 The mean value for the heat of reaction ΔU_{R} and its deviation resulting of a first point integration between 100 °C and about 290 °C of five replicate measurements. The results were normalized on the initial dry and ash-free mass and compared to the values of ΔH_{R}, determined by [5]

	ΔU_{R} $/\mathrm{J\,g_{daf}^{-1}}$	ΔH_{R} $/\mathrm{J\,g_{daf}^{-1}}$ [a]	ΔH_{R} $/\mathrm{J\,g_{daf}^{-1}}$ [b]
Mean	−715.1	−1070	−760
Deviation	±15.3	±110	±270

[a] Isothermal measurement of cellulose (240 °C, solids loading of 20 %, pH 7), performed by [5]

[b] Isothermal measurement of wood (240 °C, solids loading of 20 %, pH 7), performed by [5]

Second, the chemical composition of the used biomass from a nature protection area contains only about 30 % cellulose and a significant amount of lignin. Therefore, the released heat might differ between the determined value of [5] of about $-1070\,\mathrm{J\,g_{daf}^{-1}}$ for cellulose and the heat release calculated in this study. The enthalpy of reaction $\Delta \mathrm{H}_{\mathrm{R}}$ of lignin containing wood (Populus Tremula), which was analyzed by [5] as well, was given by $-760\,\mathrm{J\,g_{daf}^{-1}}$, which is similar to the measured heat of reaction ΔU_{R} of biomass in this study. Therefore, the composition of the biomass might have a large influence on the heat release during HTC. Additional differences in the values of Table 5 might be caused by pH value and the chosen isothermal method.

However, the experimental results show a reproducible value for the heat of reaction in a reliable range. The theoretical estimated heat release in literature shows a larger scatter than the present experimental data. To verify the experimental results of this study, one approach from literature to calculate the heat of reaction of the HTC by mass balance will be checked in the following part.

Theoretical estimation and comparison to experimental values of the heat of reaction

For each of the five reproduced experiments a reaction equation according to Eq. (9) is generated. Together with the data from elemental analysis the HHV is calculated for each coal. The mass balance for this simplified reaction equation is closed up to 97 %. Further improvements are not possible due to the simplifications on the three products. Thus, the equation should only be considered as a model. Nevertheless, this approach is used to discuss further impact on the theoretical estimation of the heat release. One of these experiments will be used as example, the values are shown in Table 6. It can be seen, that during the carbonization of $0.249\,\mathrm{g_{dry}}$ biomass about 0.01 g H_2O and $0.103\,\mathrm{g}\,CO_2$ were generated. In this case more CO_2 than H_2O is generated, which is not in agreement with [2] (molar ratio r of decarboxylation to dehydration for HTC between 0.2 and 1) and Fig. 6. The HHV increased during the hydrothermal reaction about 50 %. The estimated ΔH_R of this experiment according to Eq. (10) is about $-4402\,\mathrm{J\,g_{daf}^{-1}}$.

As specified in Eq. (6), H is composed of U and the volume work pV. Since the reaction equations are known, the difference between ΔH and ΔU will be calculated for the shown experiment in Table 6. Assumed, that in the present reaction the ideal gas law is valid, the volume work of Eq. (6) is substituted, so that the calculated value ΔH_R can be transformed to the calculated value ΔU_R^{calc1}:

$$\Delta U_R^{calc1} = \Delta H_R^{calc1} - \Delta n_R \cdot R \cdot T. \tag{11}$$

Using the new formed amount of substance Δn_R of the produced CO_2 according to Table 6, the ideal gas constant R and the maximal temperature of the reaction (300 °C), ΔU_R^{calc1} is given as $-4446\,\mathrm{J\,g_{daf}^{-1}}$. The mean value for the estimated ΔU_R^{calc1} of the five experiments is about $(-4535 \pm 215)\,\mathrm{J\,g_{daf}^{-1}}$ and therefore almost seven times higher than the measured value. As [5] showed, there might be an overestimation of the theoretical heat of reaction up to 600 % by neglecting organic byproducts in the HTC water phase and the amount of combustible gases [5].

To reduce the overestimation based on the DOM, in this present study some assumptions were applied for the estimation of ΔU_R^{calc1}. In a mass balance according to Table 6, the product suspension is dried at 105 °C . Therefore, it is assumed, that the DOM of the suspension is predominantly stored in the solid coal, although some products of the HTC are volatile at this temperature (like formic acid [14]). The energy content of these volatile compounds is neglected on the product side as well as combustible gases. Although the non volatile DOM was considered, the amount of ΔU_R^{calc1} of $-4446\,\mathrm{J\,g_{daf}^{-1}}$ is still highly overrated, as other values in literature are [1, 5]. Therefore, it can be concluded that the influence of the DOM dried on the coal to the overestimation of the heat release is relatively small and more precisely assumptions have to be done. To evaluate further influencing parameters in the estimation of ΔU_R^{calc1}, two different approaches were considered and compared to the experimental values of Table 6.

First, CH_4 is considered as combustible part in the gaseous phase instead of the assumption that the gas consists of 100 % CO_2. As known from literature, the content of CH_4 increases with time and temperature [2, 24]. As in this study the CH_4 concentration is not measured, a value from literature is taken for an assumption. In a similar experiment (wood saw dust, dry content 10 % and 303 °C pH value 9) about 23 vol% CH_4 were produced [24]. This value is taken for a calculation based on the balance in Table 6, added by CH_4. In this calculation, 23 % of the carbon which was bound in the gas (only CO_2 in that assumption) is now bound in CH_4, the rest stays in CO_2. The remaining oxygen is bound in water. Therefore, ΔU_R^{calc2} is about $-2541\,\mathrm{J\,g_{daf}^{-1}}$, whereas the mass balance is closed about 98 %.

Second, to close the mass balance, an additional molecule is generated to consider the volatiles. It consists of carbon, nitrogen, and hydrogen. The HHV of this molecule is calculated according to Eq. (5). The mass loss due to the gas lost when opening the high pressure cells is defined as the mass of the produced CO_2. As done before, 23 % of the carbon which was bound in the gas is stored in CH_4. Via mass balance, the remaining oxygen amount is bound in water. In this case, ΔU_R^{calc3} is about $-922\,\mathrm{J\,g_{daf}^{-1}}$.

The different estimated values for ΔU_R^{calc} are summarized in Fig. 8. Due to the fact that all estimated values are based on assumptions, there is a large range of values between -4446 and $-922\,\mathrm{J\,g_{daf}^{-1}}$, comparable to the range of values known from literature [1, 4, 6]. The more HTC products like DOM or combustible gases were considered, the less the deviation to the experimentally determined value ΔU_R^{exp} is. At the same time, the effort increases.

Table 6 Example for the mass balance: the process water is dried completely, only volatile compounds (at 105 °C) and energy rich gaseous compounds were neglected. This approach is based on the measured values in the experimental setup. ΔU_R^{calc1} is calculated according to Eqs. (10) and (11)

	Biomass	→	Coal + DOM (dried)	+	CO_2	+	H_2O
	$0.314\ C_{32.2}H_{52.2}NO_{21.4}$	→	$0.286\ C_{27.2}H_{25.2}NO_{5.3}$	+	$2.35\ CO_2$	+	$0.5\ H_2O$
M/g mol $^{-1}$	794.35		450.1		44		18
n/mmol	0.314		0.286		2.35		0.5
$m/\mathrm{g_{daf}}$	0.2494		0.1287		0.1034		0.0101
HHV/MJ $\mathrm{kg_{daf}^{-1}}$	19.79[a]		29.82[b]		–		–
			$\Delta U_R^{calc1} = -4446\,\mathrm{J\,g_{daf}^{-1}}$				

[a] HHV measured according to DIN 51900-2

[b] HHV calculated according to [11]

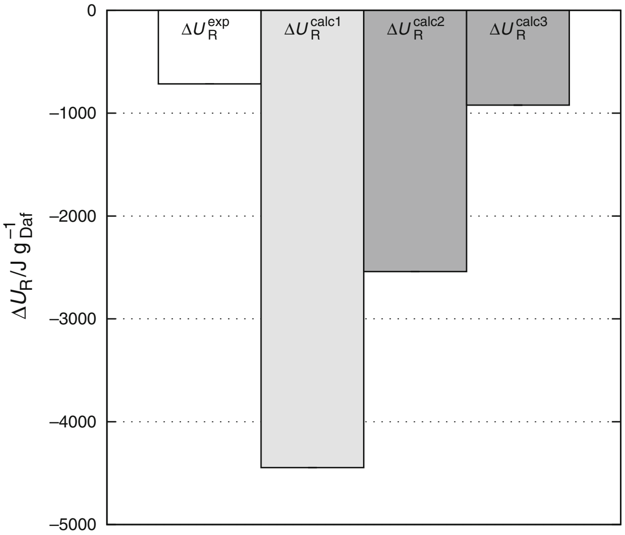

Fig. 8 Comparison of $\Delta U_R^{\mathrm{exp}}$ and three calculated values: $\Delta U_R^{\mathrm{calc1}}$ is calculated according to measured values of Table 6; $\Delta U_R^{\mathrm{calc2}}$ is estimated by an assumption for additionally formed CH_4; $\Delta U_R^{\mathrm{calc3}}$ is estimated by assuming values for CH_4, CO_2, H_2O and an additional molecule to close the mass balance

In contrast to the calculations, DSC measurements provide information about the time and temperature dependence of the heat release. Therefore, theoretical estimations cannot replace experimental measurements.

Conclusions

Up to now, there was no publication with a comparison of estimated and measured values for the heat of reaction of the hydrothermal carbonization. The values from theoretical estimations in the literature differ in a wide range from $-5.8\,\mathrm{MJ\,kg^{-1}_{feed,dry}}$ up to zero [1, 6, 8] and therefore they mostly do not fit to the experimental values. The presented procedure is developed to compare experimental and estimated values from the same experiment. For this, a heat flow DSC in temperature scanning mode is used for heat of reaction measurements, while before in HTC experiments isothermal mode is chosen in most cases [5, 9, 10]. The utilization of the C80 DSC allows (a) the usage of the glass containers, which are necessary for balancing the experiment; (b) to produce enough HTC-coal for an analysis of the C, H, and N values of the product. These values are needed to calculate the HHV of the product and hence the heat of reaction using the simplified law of Hess.

The results show that

1. The impact of the glass container on the shape of the curve (used as indicator for the temperature of the exothermic reactions) is given, but can be neglected.
2. A different experimental setup with empty reference cells can be used to get results in the error range of the setup from ISO 11357-1:2009 using water in the reference cell. With this setup, the experimental effort can be strongly reduced for larger test series.
3. The heat of reaction experiments in temperature scanning mode and the chosen setup result in reproducible heat flow curves and elemental compositions of the products. As there is no publication on reproducibility of HTC yet, this is an interesting result.
4. For the analyzed biomass, the heat release ΔU_R is about $(-715.1 \pm 15.3)\,\mathrm{J\,g^{-1}_{daf}}$. Thus, it is in the range of [5], although there the isothermal mode is used and therefore the values of these different DSC modes can not be directly compared. With this result, the temperature scanning mode seems to be expedient as well as the isothermal mode. This was expected as in each case the time of reaction was chosen in such a way that the main thermal effects are finished (according to [5]).
5. The comparison of the experimental value with the estimated results presented in this publication shows the impact of theoretical estimations and their assumptions. Three attempts are presented.

- As it is known from [8], the water phase has a big influence on carbon balance and therefore on the energy balance, too. Thus, the first attempt was to consider the DOM by drying it on the coal. Nevertheless, this attempt leads to unsatisfying results. It has to be clarified, whether the process of drying is suited for considering the DOM or if energy is lost by volatiles.
- With the attempt to close the mass balance, the ratio r of produced CO_2 to produced H_2O is not in the expected range. The changes due to the consideration of methane show that the accuracy of this (and perhaps any) method of theoretical estimation might be highly temperature depending, as the temperature range here goes up to 290 °C and the production of gas as well as the share of methane increases rapidly at temperatures of about 240 °C [25, 26]. In addition, the composition of the biomass might have a large influence on the heat of reaction during HTC.
- With further assumptions that include volatiles and CH_4 in the gaseous phase, the theoretically estimated value of $\Delta U_R^{\mathrm{calc3}}(-922\,\mathrm{J\,g^{-1}_{daf}})$ reaches the order of the measured value. But these calculations need a lot of assumptions that are not based on measurements. Further improvements are to be made.

This shows that there are many ways and dependencies for theoretical calculations, what explains the wide range of calculated values in the literature of about $-5800\,\mathrm{J\,g_{dry}^{-1}}$ to nearly zero [1, 6, 8]. Therefore, heat of reaction measurements are indispensable for the process of HTC. The presented setup is suited for such experiments and may help to improve the theoretical estimations.

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